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(54) EASILY ADHESIVE STRETCHED FILM OF SYNDIOTACTIC POLYSTYRENE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an easily adhesive stretched film of a syndiotactic polystyrene which shows excellent adhesive properties between a film and an adhesive modified layer, and has excellent economical efficiency, recycling properties and environmental adaptability during manufacturing. SOLUTION: This easily adhesive stretched film of a syndiotactic polystyrene is obtained by laminating an adhesiveness modified layer formed of a water- dispersible copolymer polyester with a glass transition temperature of 30°C or lower, on at least one side of the stretched film composed of a styrene polymer substantially having a syndiotactic structure. Especially the adhesiveness modified layer is preferably formed by applying an aqueous dispersion of a copolyester to an unstretched film or a uniaxially stretched film, and uniaxially or biaxially orienting the film once or more before thermally treating it.

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- 2.**** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a syndiotactic polystyrene system oriented film and the easily-adhesive syndiotactic polystyrene system oriented film which was excellent in the adhesion of this film and an adhesion reforming layer in more detail. [0002]

[Description of the Prior Art]A syndiotactic polystyrene system oriented film is excellent in easy cleavability, heat resistance, an electrical property, transparency, etc., and deployment is expected from various kinds of film applications, such as an object for magnetic tape, a photograph and the object for platemaking, an object for capacitors, and an object for a package.

[0003]When using a film as wrapping especially, if needed at least on one side of an oriented film generally A printing layer, The gas barrier layer etc. which vapor-deposited the gas barrier layer, inorganic matter, or metal which carried out spreading lamination of the organic high polymer are laminated, After laminating adhesives furthermore, it is considered as the layered product which provided the sealant layer etc. with the dry laminate method or extrusion laminating method, a bag is produced using this layered product, an opening is heat sealed after filling it up with contents, and general consumers are provided with foodstuffs, medicine, sundry articles, etc. by which the sealing package was carried out. Therefore, since the above-mentioned layered product is constituted, in order to acquire sufficient adhesive property with a printing layer, a gas barrier layer or a sealant layer, etc. to an oriented film, providing physical processings and adhesive reforming layers, such as corona treatment, is generally made.

[0004]After it carries out corona treatment of the film surface to JP,H5-338089,A also in a syndiotactic polystyrene system oriented film and it makes surface tension high, an anchor coat agent is applied, and providing a sealant layer on it is indicated. However, in the case of corona discharge treatment, there is a problem to which workability falls that it is easy to carry out semipermanent electrification of the film after processing, and an adhesive property was not able to be referred to as enough, either. JP,2000-6330,A has disclosed laminate the adhesive reforming layer which consists of a self crosslinkability polyester system graft copolymer in order to improve an adhesive property with a gas barrier layer or a sealant layer to a syndiotactic polystyrene system oriented film. However, since an adhesive reforming layer was a cross-linking polymer, remelting extrusion is difficult for this film, and there was a problem in recycling efficiency.

[0005]Sliding on a syndiotactic polystyrene system oriented film by the coat method, and, providing the

reforming layer of the improvement sake in a sex or *****-proof on the other hand, Although indicated by JP,H3-109453,A, JP,H3-109454,A, JP,H8-39741,A, JP,H8-48008,A, JP,2000-6330,A, etc., it was not able to be said that the adhesive property of the reforming layer and film which are used was enough.

[0006]

[Problem to be solved by the invention]In the case of the Sindi nerd CHIPPORI styrene system oriented film, it was difficult to provide a satisfying adhesive reforming layer. For example, when using the conventional drainage system paint, sufficient adhesion of this film and an adhesive reforming layer is not acquired for character, like surface energy is [the surface of this film] low, and a degree of crystallinity is high. On the other hand, it is not preferred from a viewpoint of environmental contamination or a worker's industrial hygiene to use the paint of a solvent system.

[0007]An object of this invention is to provide the lamination syndiotactic polystyrene system oriented film excellent in the adhesion of a film and an adhesive reforming layer. It aims at providing the easily-adhesive syndiotactic polystyrene system oriented film which was excellent in economical efficiency, recycling efficiency, and the environmental suitability at the time of manufacture.

[0008]

[Means for solving problem]This invention persons were able to make the above-mentioned purpose attain in laminating the adhesive reforming layer constituted from specific moisture powder type copolymerized polyester by at least one side of this film, as a result of inquiring wholeheartedly. Namely, this invention, It is the easily-adhesive syndiotactic polystyrene system oriented film in which the adhesive reforming layer where the glass transition point was constituted from moisture powder type copolymerized polyester 30 ** or less by at least one side of the oriented film which consists of a styrene system polymer which has syndiotactic structure substantially was laminated. The adhesive reforming layer where the desirable mode comprised above-mentioned moisture powder type copolymerized polyester, After applying the aqueous coating fluid containing moisture powder type copolymerized polyester to the unstretched film or uniaxial stretched film which consists of a styrene system polymer which has syndiotactic structure substantially, Subsequently, after extending once or more to 1 shaft orientations or 2 shaft orientations, it is an easily-adhesive syndiotactic polystyrene system oriented film formed by heat-treating.

[0009]

[Mode for carrying out the invention]As a styrene system polymer which has the syndiotactic structure of this invention, The tacticity by which the phenyl group or substituted phenyl group of a side chain is quantified with a nuclear magnetic resonance method as syndiotactic structure by die ADDO (a constitutional unit is two pieces) Not less than 85%, Polystyrene which is not less than 50% of SHINJIO bamboo tick structure in a pentad (a constitutional unit is five pieces), poly (p-, m-, or o-methylstyrene) and poly (2, 4-, 2, and 5-.) Poly, such as 3,4- or 3,5-dimethylstyrene, and poly (p-tertiary-butylstyrene) (alkyl styrene), Poly (p-, m-, or o-chlorostyrene), poly (p-, m-, or o-bromostyrene), Poly, such as poly (p-, m-, or o-fluorostyrene) and poly (o-methyl -p-fluorostyrene) (halogenation styrene), poly (alkoxy styrene), such as poly (halogenation alkyl styrene), such as poly (p-, m-, or o-chloromethyl styrene), poly (p-, m-, or o-methoxy styrene), and poly (p-, m-, or o-ethoxystyrene), and poly (p-) Poly, such as m- or o-carboxymethylstyrene (carboxy alkyl styrene), poly (alkyl silylstyrene), such as poly (alkyl ether styrene), such as poly (p-vinylbenzyl propyl), and poly (p-trimethylsilyl styrene), -- poly (vinylbenzyl dimethoxyphosphide) etc. are mentioned further. Especially syndiotactic polystyrene is preferred.

[0010]The styrene system polymer in which this invention has syndiotactic structure substantially, It is not necessary to be necessarily a single compound, and although a mixture, and copolymers and those mixtures with the polystyrene system polymer of atactic structure or isotactic structure may be sufficient, the styrene system polymer which has syndiotactic structure at least 40weight % or more is comprised.

[0011]The weight average molecular weight of the syndiotactic polystyrene system polymer of this invention is 50,000 or more still more preferably 10,000 or more. Weight average molecular weight cannot obtain the biaxially oriented film excellent in the strong ductility characteristic or heat resistance in less than 10,000 thing. Although not limited in particular for the maximum of weight average molecular weight, since generating of the fracture accompanying the increase in the load of an extruder and the increase in extension tension, etc. arise, it is not desirable at 1500 or 000 or more.

[0012]various publicly known add-in material, for example, lubricant, paints, heat stabilization material, the antioxidant, the spray for preventing static electricity, the shock-proof improving agent, etc. may be added in the range which does not check the effect of this invention by the syndiotactic polystyrene system polymer of this invention. As lubricant, inertness particles are mentioned to syndiotactic polystyrene system polymer, such as particles which consist of metal salt or organic polymer, such as metallic oxides, such as silica, a titanium dioxide, talc, and kaolinite, calcium carbonate, calcium phosphate, and barium sulfate. Two or more sorts may be used together, using any one sort of the above-mentioned lubricant independently.

[0013]The syndiotactic polystyrene system oriented film of this invention can be manufactured by a publicly known method. For example, the serial biaxial-stretching method of performing vertical extension and lateral orientation for the unstretched film which obtained it from the dice by carrying out melt extruding cooling solidification of the syndiotactic polystyrene system resin to film state in order is applicable. In addition, the simultaneous biaxial-stretching method of performing simultaneously serial extension methods, such as width and a vertical serial biaxial-stretching method, length, width and the vertical serial extending method, length, length, the horizontal serial extending method, vertical extension, and lateral orientation etc. can be adopted, and an extension method can be chosen according to various characteristics demanded, such as intensity and dimensional stability. The uniaxial stretched film by the vertical uniaxial-stretching method and a horizontal uniaxial-stretching method may be sufficient. As a stretching device, a roll drawing machine, a tenter drawing machine, an inflation drawing machine, etc. can be used. As for the film after extension, it is preferred to heat-treat heat setting processing, vertical relaxation processing, horizontal relaxation processing, etc. at the point whose thermal dimensional stability, adhesive property, etc. improve.

[0014]As a method of establishing the adhesive reforming layer which comprised moisture powder type copolymerized polyester in a syndiotactic polystyrene system oriented film, For example, after applying and drying the aqueous coating fluid containing moisture powder type copolymerized polyester at an unstretched film or an uniaxial stretched film and extending once or more subsequently to 1 shaft orientations or 2 shaft orientations, the method (the in-line coat method) of heat-treating is mentioned. The coating liquid of the drainage system which contains water dispersibility straight chain type polyester in the film which carried out extension and heat treatment in-line one or off-line may be applied and dried. The in-line coat method is preferred also at the point whose adhesion of a film and an adhesive reforming layer can manufacture inexpensive and also improves. Although a publicly known coating system is applicable

as a coating method, the roll coat method, the air knife method, and the bar coat method are mentioned, for example.

[0015]The water dispersibility in moisture powder type copolymerized polyester of this invention means the polyester which the rate of water distributes [soluble or] to the inside of the aqueous coating fluid which is 20 weight % or more. The main ingredients of aqueous coating fluid are water containing an alkaline aqueous solution, aqueous acids, an organic solvent, or a surface-active agent, for example. The water dispersibility of straight chain type polyester is revealed by introducing a hydrophilic radical into the main chain of polyester, for example. As a hydrophilic radical, $-\text{NH}_2$ group, $-\text{OH}$ radical, a $-\text{CO}_2\text{M}$ basis, a $-\text{SO}_3\text{M}$ basis (M shows cations, such as hydrogen, the 1th periodic table II, group III elements, and ammonium), etc. are mentioned.

[0016]The glass transition temperature of moisture powder type copolymerized polyester in this invention needs to be 30 °C or less, and is 10 °C or less more preferably. By using moisture powder type copolymerized polyester which is the glass transition temperature of 30 °C or less, the adhesion of a syndiotactic polystyrene system film and an adhesive reforming layer improves remarkably.

[0017]Since this adhesive reforming layer has enough adhesion with printer's ink, the anchoring agent for a sealant lamination, etc., In the layered product which provided the ink layer and the laminate layer in the adhesive reforming layer side, it becomes possible to improve the adhesion of a syndiotactic polystyrene system oriented film, and an ink layer and a sealant layer.

[0018]moisture powder type copolymerized polyester of this invention is a publicly known method, and polymerizes from dicarboxylic acid and/or its derivative, diol, its derivative, hydroxy acid, and/or its derivative, although things can be carried out, As a method of obtaining moisture powder type copolymerized polyester which is the glass transition temperature of 30 °C or less, a method of setting up appropriately a kind and a ratio of aliphatic dicarboxylic acid to aromatic dicarboxylic acid about a dicarboxylic acid component is mentioned, for example. For example, a method of carrying out an aliphatic dicarboxylic acid component 30-100-mol% of total dicarboxylic acid components, and carrying out copolymerization of the aromatic dicarboxylic acid component at 70-0-mol% of a rate of a total dicarboxylic acid component is mentioned as diol of the carbon numbers 2-6 as main ingredients of diol.

[0019]As an aliphatic dicarboxylic acid component, succinic acid, adipic acid, azelaic acid, sebacic acid, dodecane dione acid, dimer acid, 1, and 4-cyclohexanedicarboxylic acid etc. are mentioned. In this invention, alicyclic dicarboxylic acid shall be included in aliphatic dicarboxylic acid. As aromatic dicarboxylic acid, terephthalic acid, isophthalic acid, 2, and 6-naphthalene dicarboxylic acid etc. are mentioned.

[0020]As diol, ethylene glycol, 1,4-butanediol, neopentyl glycol, 1,4-cyclohexane dimethanol, a diethylene glycol, triethylene glycol, a polyethylene glycol, a PORIE truck methyleneglycol, etc. are mentioned. Copolymerization of the hydroxy acid ingredients, such as oxycaproic acid, may be carried out.

[0021]As a monomer with a hydrophilic radical for giving water dispersibility, although 5-sulfoisophtharate metal salt, sulfoterephthalic acid metal salt, etc. are mentioned, it is not limited to these.

[0022]Although a monomer which had three or more functional groups in intramolecular may be used as a raw material monomer of moisture powder type copolymerized polyester of this invention, since the recycling efficiency of a laminated film gets worse, it is preferred that it is less than 3 mol % to dicarboxylic

acid, and all the the diol numbers of mols.

[0023]As a method of obtaining a dispersing element of moisture powder type copolymerized polyester, a method of distributing in water, for example with polar solvents is mentioned. For example, the above-mentioned polyester and polar solvents are beforehand mixed at 50-200 **, and a method of adding water to this mixture or a method of making the above-mentioned polyester, polar solvents, and water live together, and stirring and distributing at 40-120 ** is mentioned, stirring. As polar solvents, solvents, such as an alcohol system, an ester system, a ketone system, and an amide system, can be mentioned. Surface-active agents, such as alkylbenzene-sulfonic-acid soda, alkyl naphthalene sulfonic acid soda, alkyl-sulfonic-acid soda, and alkyl ether sulfonic acid soda, can also be used instead of polar solvents. The above-mentioned polar solvents and a surface-active agent are independent, or it can combine and they can be used as a partially aromatic solvent. A water dispersing element of polyester distributed with a described method can be further diluted with mixed liquor of water or water, and a polar solvent, and can be used as aqueous coating fluid to a film. Alcohols, such as ethyl alcohol and isopropyl alcohol, are mentioned as the above-mentioned polar solvent for dilution. From industrial-hygiene nature, the danger of a fire and explosion, etc., 20 weight % or more is desirable still more preferred, and concentration of water in coating liquid at the time of applying to a film is 50 weight % or more.

[0024]Thickness of an adhesive reforming layer of this invention is 0.01 micrometer - 5 micrometers, and is 0.05 micrometer - 1 micrometer preferably. If thickness of an adhesive reforming layer is too thin, sufficient adhesive property will not be acquired. If thickness of an adhesive reforming layer is too thick, an excessive coating agent and a dryer are needed superfluously and it is not economical. Since it generates also when an adhesive property gets worse, it is not desirable.

[0025]Although moisture powder type copolymerized polyester of this invention can form an adhesive reforming layer independently, Polyester system resin general-purpose from other purposes, urethane resin, an acrylic resin, Conductive resin and antimicrobial resin, such as those copolymers, various moisture powder resin, etc. various function nature resin, for example, poly aniline, and polypyrrole, ultraviolet absorbability resin, and gas-barrier resin may be mixed, and an adhesive reforming layer may be formed. An adhesive reforming layer can be made to contain additive agents, such as a spray for preventing static electricity, inorganic lubricant, organic lubricant, and an ultraviolet ray absorbent, in the range which does not spoil an effect of this invention.

[0026]Since an adhesive reforming layer of this invention is excellent in adhesion with a syndiotactic polystyrene system oriented film and also fully has adhesion with printer's ink, an anchoring agent for a sealant lamination, etc., When a layered product which provided an ink layer and a laminate layer in the adhesive reforming layer side is produced, laminate strength and seal strength of a layered product improve remarkably.

[0027]

[Working example]Hereafter, this invention is not limited by these embodiments although an embodiment explains this invention concretely. The following methods measure and estimate the characteristic shown in an embodiment.

[0028](1) The gauze first washed and dried with clear acetone whenever [glass transition Atsushi / of moisture powder type copolymerized polyester] is prepared, acetone is attached to the gauze, and the adhesive reforming layer of the film was rubbed. SOKUSURE extraction was carried out by the following

condition from the gauze, DSC measurement of the sample which separated and hardened the improved adhesiveness layer by drying was carried out by the following condition, and it asked for the glass transition temperature T_g based on JIS K 7121.

(ソックスレー抽出条件)

溶媒 ; アセトン

湯浴温度 ; 95℃

(DSC測定条件)

装置名 ; MacScience社製DSC3100

パン ; アルミパン (非気密型)

試料重量 ; 4mg

昇温開始温度 ; -100℃

昇温速度 ; 20℃/min.

雰囲気 ; アルゴン

[0029](2) the adhesion evaluation with a film and an adhesive reforming layer -- the tape friction test shown below estimated the adhesion of a syndiotactic polystyrene system film and an adhesive reforming layer. The double-sided tape (Product No[made from Japanese Toden material] .535A) of 50mmX60mm size was stuck on the glass plate, on it, the spreading side was made into the upper part and the syndiotactic polystyrene system oriented film in which the adhesive reforming layer was laminated was stuck. Next, the abbreviation half of 24 mm in width and 100 mm in length a cellophane tape (CT-24 by Nichiban Co., Ltd.) is stuck on the field of an adhesive reforming layer, After forcing and sticking the portion which the cellophane tape stuck by the curved surface part which bent polytetrafluoroethylene plate manufacturing 2 mm in thickness, 30 mm in width, and 100 mm in length, Rapid exfoliation of the cellophane tape was carried out 90 degrees by hand at the direction, the exfoliation part was observed visually, the case where a glue line did not exfoliate was considered as O, the case where it exfoliated was made into x, and the quality of the adhesion of an adhesive reforming layer and a syndiotactic polystyrene system film was judged.

[0030](2) In accordance with evaluation of printability, next a shown valuation method, the printability (a wettability and adhesion of ink) of a syndiotactic polystyrene system film was evaluated. A specimen of A-4 size (210 mm x 297 mm) was prepared, gravure ink (TOYO INK MFG. CO., LTD. make NEW fine R39 indigo blue) was applied to the adhesive refining side side of the specimen 3 micrometers in thickness, and 90 ** dried for 120 seconds. Commercial gravure ink was diluted with a diluting solvent (NF102 by TOYO INK MFG. CO., LTD.) to gravure ink for an examination, and what carried out viscosity preparation was used for it. Viscosity of gravure ink was measured using #3 ZAN cup, and as it had been viscosity 17 seconds, it carried out viscosity preparation. What has O and crawling in a thing without crawling of ink by the above evaluation was made into x. The same friction test as (1) estimated the adhesion of an ink layer. What not exfoliating was made into O and what exfoliating was made into x.

[0031](Embodiment 1) Moisture powder type copolymerized polyester (Toyobo Co., Ltd. make BAIRO knurl MD-1930) was diluted with water:isopropyl alcohol =9:1 (weight ratio) so that it might become 10% of solids concentration, and coating liquid was prepared. After mixing a polymer chip which added a bridge construction polystyrene particle with a mean particle diameter of 2 micrometers 2.0weight % to 100 weight % of syndiotactic polystyrene (weight average molecular weight 300,000) as lubricant, and a polymer chip with which lubricant is not added at a rate of 1 to 9 by a weight ratio, It dried, melting was carried out at 295

**, it extruded from a T die with a lip gap of 500 micrometers, adhesion and cooling solidification made it a 40 ** cooling roller by the air knife method, and a 240-micrometer unstretched film was obtained. [0032]Preheat an unstretched film at 110 ** with a roll first, and it extends 3.3 times to a lengthwise direction between rolls with the speed difference heated at 120 **, Subsequently, vertical relaxation processing is performed 12% between a 150 ** ceramics roll and a 40 ** metallic roll, Subsequently, the aforementioned coating liquid was applied by the die coater system, it dried by a 70 ** hot wind, the film was further preheated at 110 ** by the tenter, it extended 3.5 times at the extension temperature of 120 ** in the transverse direction, and heat setting was carried out for 10 seconds at 265 **. Then, horizontal relaxation processing was carried out 5% at 230 **, vertical relaxation processing was carried out 3% between a 220 more ** ceramics roll and a 40 ** metallic roll, and 20-micrometer-thick biaxial-stretching syndiotactic polystyrene films were obtained. Final coating agent coverage was 0.1g / m². The evaluation result of these obtained syndiotactic polystyrene films was shown in Table 1.

[0033]
[Table 1]

	接着性改質層の水分散型共重合ポリエステル	T _g (℃)	接着性改質層の密着性	印刷性	
				はじき	密着性
実施例 1	パイロナール MD-1930	-7	○	○	○
実施例 2	パイロナール MD-1985	-17	○	○	○
比較例 1	パイロナール MD-1200	70	×	○	×
比較例 2	パイロナール MD-1500	79	×	○	×
比較例 3	なし		—	×	×

[0034](Embodiment 2) As moisture powder type copolymerized polyester, except having used moisture powder type copolymerized polyester (Toyobo Co., Ltd. make BAIRO knurl MD-1985), it is the same method as an embodiment, and syndiotactic polystyrene films were obtained. The evaluation result of the obtained film was shown in Table 1.

[0035](Comparative example 1) As moisture powder type copolymerized polyester, except having used moisture powder type copolymerized polyester (Toyobo Co., Ltd. make BAIRO knurl MD-1200), it is the same method as an embodiment, and syndiotactic polystyrene films were obtained. The evaluation result of the obtained film was shown in Table 1.

[0036](Comparative example 2) As moisture powder type copolymerized polyester, except having used moisture powder type copolymerized polyester (Toyobo Co., Ltd. make BAIRO knurl MD-1500), it is the same method as an embodiment, and syndiotactic polystyrene films were obtained. The evaluation result of the obtained film was shown in Table 1.

[0037](Comparative example 3) Except not applying an adhesive reforming layer, it is the same method as

an embodiment, and the syndiotactic polystyrene system film was obtained. The evaluation result of the obtained film was shown in Table 1.

[0038]

[Effect of the Invention]By this invention, the composition as a description is adopted as Claims as above. Therefore, the syndiotactic polystyrene system oriented film excellent in the adhesion of a syndiotactic polystyrene system film and an adhesive reforming layer is provided.

Since an adhesive reforming layer can be laminated by the in-line coat method in a film manufacturing process, it is economical, and since coating liquid is a drainage system, it excels also in the danger of a fire, or the field of work environment. Recycling of the made film is also possible.

[Translation done.]